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SURFACE STUDIES OF ANODIC ALUMINUM OXIDE LAYERS FORMED IN PHOSPHORIC ACID SOLUTIONS

MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

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Neil T. McDevitt
Project Engineer

FOR THE DIRECTOR

S. W. Tsai, Chief
Mechanics & Surface Interactions Branch
Nonmetallic Materials Division

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Phosphoric acid generates a composite oxide with a dense, nonporous layer forming on the aluminum anode, and then a porous layer forming on top. The nonporous layer forms a continuous film and should offer the most protection to the bulk metal. Our objective in this study was to determine the properties and growth characteristics of this nonporous layer under the

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20. (Abstract, continued)

influence of voltage and concentration of electrolyte.

9. PERFORMING ORGANIZATION (continued)

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FOREWORD

This technical report was prepared by Neil McDevitt, William L. Baun and Gary Fugate, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright-Patterson Air Force Base, Ohio and Mr. James S. Solomon, University of Dayton Research Institute, Dayton, Ohio. The work was initiated under Project 2419, "Nonmetallic and Composite Materials", and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

This report covers work conducted inhouse during the period July 1975 through September 1976. The report was released by the author in March 1977.

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SUMMARY

The aircraft industry has become interested in using adhesively bonded aluminum alloys as primary structural materials. One of the most critical characteristics of a bonded panel is its anticipated life expectancy. Researchers have observed that the surface preparation of the aluminum metal prior to bonding greatly influences the durability of the bondline. Therefore, continuing research is necessary in the area of surface preparation to improve the quality of the bondline.

The surface preparation of current interest is anodization by phosphoric acid electrolyte. The current process calls for a 10-volt anodization. The approach for this study was an empirical one where the applied potential was 30 and 60 volts. This electrolyte generates a composite oxide with a dense, nonporous layer forming on the aluminum anode, and then a porous layer forming on top of the nonporous layer. The nonporous layer forms a continuous film and should offer the most protection to the bulk metal.

The prepared aluminum surfaces were exposed to a phosphoric acid electrolyte at an applied potential of 30 volts and 60 volts, at a concentration of 0.1M and 1.0M. Specimens were removed from the anodization bath at 5, 30, 90, and 300 seconds. The thickness and refractive index of the oxide layers were determined by ellipsometry. The average refractive index generated by these times was 1.55, 1.64, 1.50, and 1.4. Transmission electron micrographs show the oxide layer with a refractive index of 1.64 to be nonporous. This nonporous layer increases in thickness from 330 to 860 $\overset{\circ}{A}$, as concentration and voltage increases. Auger electron spectroscopy was useful in making a quick estimate of oxide thickness while profiling the film to determine the elements present. Surfaces generated by this study were difficult to characterize using ion scattering and secondary ion mass spectroscopy.

SECTION I

INTRODUCTION

Researchers have observed that the single most critical parameter influencing bond strength and durability of adhesively bonded aluminum structures is the surface preparation of the metal before bonding. The surface preparation of current interest for aluminum alloys, to be used as primary structural materials on aircraft, is anodization.

The process of anodization produces a coating of metal oxide or hydroxide by the electrochemical oxidation of a metal anode in contact with an electrolyte. This type of oxidation is limited to a few metals, and the one metal most employed for this process is aluminum. The electrolytes used in commercial processes are strongly acidic and normally generate a composite film. The composite film consists of a nonporous (barrier) layer forming directly on the aluminum anode, and then a porous layer forming on top of the barrier layer (Reference 1). In order to protect the aluminum metal surface the process should produce a continuous oxide film. The barrier layer oxide film is usually continuous, while the porous layer is essentially noncontinuous with the pore structure extending through this oxide layer (Reference 2). Porous anodic oxide films formed on aluminum by numerous electrolytes have received attention in a number of review articles (References 3, 4, and 5) and will receive only general mention in this report. The commercial process of anodization that produces a thick ($>2.5\mu m$) porous oxide film, that resists weathering and deterioration, is well known (Reference 6). However, in order for an adhesive to form an integral bond with the metal adherend, the surface oxide layer has to be thin ($<0.5\mu m$). The quality of this thin anodic oxide film will determine the amount of corrosion protection the bulk aluminum will receive and; therefore, add to the durability of the formed adhesive bond.

This report is primarily concerned with the formation of porous anodic films on aluminum using phosphoric acid as the electrolyte, since this acid is creating the most interest, at present, for the surface preparation of aluminum alloys used in bonded aircraft structures. In particular, our interest is in the early stages of oxide growth, since this is the layer that forms a continuous film and should offer the most protection to the bulk metal. Conditions being used presently for anodizing aluminum with phosphoric acid are 10V, 1.0M for 20 minutes. Oxide films grown under these conditions have been studied (References 7 and 8). In order to expand our knowledge on oxide films grown in a phosphoric acid electrolyte, our conditions differed from those stated previously.

A number of surface analysis techniques were utilized to help us better understand the characteristics of these oxide layers. With these data it should be possible to develop improved anodic oxide films by calculation of the desired properties rather than by trial and error.

SECTION II

EXPERIMENTAL

The study was carried out using vacuum deposited (10^{-5} torr) aluminum films (0.5μm) on chemically cleaned glass slides. The deposition rate was 100 Å/sec while the slides were held at 150°C. Films deposited under these conditions are very homogeneous in coverage and provide a surface that is both suitable for anodization and ellipsometry studies.

Each specimen was masked to present a 10 cm^2 area to the electrolyte. The surfaces were then exposed to 0.1M and 1.0M H_3PO_4 electrolyte under an applied potential of 30 and 60 volts. Specimens were removed from the electrolyte after 5, 30, 90, and 300 seconds.

All ellipsometry measurements were made on each "bare" aluminum film prior to anodization and after each time interval in the electrolyte. Data was obtained at an angle of incidence of 70° using an unpolarized light source of 5461 Å wavelength. Experimental details are described in a previous report (Reference 9).

Ion Scattering Spectroscopy (ISS), Secondary Ion Mass Spectroscopy (SIMS), and Auger Electron Spectroscopy (AES) were utilized in studying the elemental chemical properties of the anodized surfaces. The basis for these techniques depends primarily on bombarding a solid surface with a beam of charged particles under high vacuum and detecting the energy and/or mass of the particles emitted or reflected from the surface. ISS involves bombarding the surface with rare gas ions and then detecting the energy losses of the ions reflected from the first monolayer of the sample. Simultaneously, these bombarding ions will sputter off the first atomic layer with a small fraction being ejected as positive ions. These secondary ions are then directed into a small quadrupole mass spectrometer and

detected to give an elemental mass spectrum (SIMS). AES uses an electron beam for probing the solid surface and analyzes the energy distribution of the secondary electrons created in the process. Depth profiles of these surfaces are easily obtained in the Auger technique by sputtering the surface with a heavy (Ar) rare gas ion while probing with the electron beam. Discussion of these techniques may be found in earlier publications (References 10, 11, and 12).

Transmission Electron Micrographs (TEM) were obtained on most of the anodized surfaces.

SECTION III

RESULTS AND DISCUSSION

1. CHARACTERISTICS OF FILM GROWTH

In order to utilize ellipsometry in a study of this nature, it is
necessary to know the optical constants, $n_c = \eta (1-i\kappa)$, of the "bare" metal
surface (considered to be film free[*]). The optical properties and thickness
of an oxide film generated by the electrochemical process may then be
determined. The problems encountered in preparing aluminum on glass
slides have been discussed (References 13 and 14); therefore, it was
necessary to determine the optical constants of all the prepared metal
surfaces. In this manner all of the surface imperfections are taken into
consideration when we determine film thickness. The average refractive
index was determined to be, $n_S = 0.8338 \pm 0.1 (1 - i\ 5.8372 \pm 1.0)$; however,
the refractive index of each individual sample was used in the final analysis.
The optical constants of the generated anodic oxide films were obtained by
trial and error fitting of the experimental and calculated data. The calcu-
lated data was obtained with the use of a computer program. The experi-
mental data obtained from the ellipsometer is observed as $\triangle$ and ψ values.

Figure 1 shows the type of curve that would be generated by an anodic
oxide film of boehmite (Al 00H, refractive index of 1.65) on an aluminum
film having an optical constant reported previously. Actual experimental re-
sults obtained on an oxide film from a phthalic acid electrolyte fall quite
close to this curve. The perpendicular mark represents the "bare" sub-
strate and the data follows a clockwise motion. The phthalic acid electro-
lyte gave a thickness of 1020 Å at 80 volts. The average refractive index
of the five anodic oxide films obtained from this electrolyte was 1.647 ± 0.007.
Using these optical constants the curve will retrace itself, starting around
2100 Å, when the film does not absorb the 5461 Å source energy ($\kappa = 0$).

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[*] A natural air formed oxide, ~20 Å, is usually present.

The chemistry and crystal structure of aluminum oxide and hydroxide films on aluminum have been studied extensively (Reference 4). For most of the previous studies the conclusions about formed oxide films vary from amorphous barrier layers to crystalline porous layers. Calculated ellipsometry curves in Figure 2 show Al-O compounds that range in refractive index from 1.58 to 1.76. An analysis of these results shows it is not possible to differentiate the three compounds in the thickness range 0 to 500 Å. The thickness region 1300 to 2100 Å would show similar overlap. Experimental results, obtained diligently, could differentiate between bayerite and boehmite in the thickness region 500 to 1300 Å. However, these data were calculated on the premise that only a single film, with a homogeneous refractive index, has grown on the aluminum substrate. Research in this area, using phosphoric acid as the electrolyte, shows that we cannot use the above premise (Reference 15). The fact that composite films grow in phosphoric acid and the refractive index will not be homogeneous throughout the film thickness can be seen in the transmission electron micrographs shown in Figures 3 and 4. Also shown is the different morphologies for the barrier and porous layers obtained from each electrolyte concentration.

The results of the ellipsometrically determined values of refractive index and thickness of all the films generated from this study are given in Table 1. The effect a changing refractive index would have on the ellipsometric data can be seen from the mosaic of curves shown in Figure 5.

The data, from Table I, proceeds in a clockwise direction from the perpendicular mark. The refractive index observed experimentally indicates a dense barrier layer. As the film grows thicker the best fit data for the experimental ellipsometric parameters Δ and ψ to those calculated by the computer program show the refractive index dropping in value. If the absorption coefficient (κ) remains equal to zero, the curve will retrace itself. In order to obtain a best fit for the Δ and ψ data obtained from the 300 second interval analization, κ has to assume a positive value.

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TABLE 1

VALUES OF REFRACTIVE INDEX AND THICKNESS FOR ANODIC OXIDE

FILMS

		TIME (SEC)			
		5	30	90	300
30V	η_f	1.60	1.64	1.55	1.4[‡]
0.1M	d, Å	300	330	590	860
30V	η_f	1.55	1.65	1.50	1.3[‡]
1.0M	d, Å	320	375	815	2630
60V	η_f	1.52	1.60	1.54	1.4[‡]
0.1M	d, Å	730	760	985	1765
60V	η_f	1.55	1.64	1.50	1.4[‡]
1.0M	d, Å	720	860	1030	2855

[‡] $\kappa > 0.01$

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The 300-second anodization experimental data fall close to the calculated curve, designated X, shown in Figure 6. It is apparent from these data that the porous growth decreases the value of η while it increases κ. When the observed value of κ is 0.01 or less, for films less than 1000 $\overset{o}{A}$, $\triangle$ and ψ yield approximately the same values as when $\kappa = 0$ (Figure 7).

The data shown in Figure 7 makes it obvious if we match only $\triangle$ values (experimental to calculated) it would not be possible to follow the mechanism of the porous oxide growth because these values remain constant throughout the thickness range of interest, and the sensitivity to porous growth is reflected primarily in ψ.

The relationship of anodic oxide growth rate to film thickness is shown in Figure 8 for the various anodization parameters. During the first 30 seconds the growth rate for the 60-volt anodization is approximately 2 times that of the 30 volt. The more dense barrier layer forms during this time interval and the grouping of the data points indicates the thickness of this layer is directly proportional to the applied voltage. At the 90-second interval the growth rate for the 30-volt anodization slows to the point where the 60 volt approaches the same rate. It is apparent that the mechanism of oxide growth changes during the 30-90-second anodization interval. After the 90-second interval the concentration of the electrolyte plays a more important role. This can be seen in Figure 8 for the 300-second time interval data points where the 1.0M, 30 V curve crosses the 0.1M, 60 V curve, and the growth rates for the same concentration approaches a similar value.

The average refractive index for the 5-second interval data points is 1.55. This value is somewhat low for a barrier layer film. This may be explained by the initial slight roughing of the aluminum surface in contact with the phosphoric acid. The data points from the 30-second interval show an average $\eta_f = 1.63$. This value is more in line with the refractive index of a true barrier layer.

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The average refractive index for the 90-second interval drops to 1.52. It is between the 30- and 90-second time interval where the anodic oxide growth mechanism changes from nonporous to porous. The refractive index reading for the 300-second interval is 1.38. This reading should be designated as the apparent refractive index because the absorption coefficient value exceeds 0.01.

2. AUGER CHARACTERISTICS OF ANODIC OXIDE FILMS

Constructing an in-depth profile map is a relatively easy task using Auger peaks which are repetitively recorded while simultaneously sputtering away the surface (Reference 16). The peak to peak heights of elements of interest are measured and plotted as a function of sputtering time. An arbitrary characteristic (e.g. crossover point Al_{KMM} and O profiles) of the profile curve is determined to be the end point for the disappearance of that element from the sputtered film. Using this end point, in units of time, and film thickness generated by the ellipsometer a calibration curve can be established. This curve is valid only for the energy conditions used in obtaining the Auger data. Figure 9 is a calibration curve for the data obtained from this study. The sputtering rate will be dependent on the density and stoichiometry of the film. The deviation from the straight line for this case is presumed to be primarily due to a change in density of the film as sputtering proceeds from the barrier to porous layer. The deviation indicates less time to sputter through a film as it becomes thicker. This in turn would indicate a less dense film which would be the case for a porous anodic oxide layer.

Anion incorporation into the oxide film has always been of concern to past researchers (References 17 and 18). Figure 10 shows an Auger spectrum for a 1.0M, 30 V anodization. Spectral features show phosphorous, some carbon, oxygen and aluminum. The relative intensity of the phosphorous energy peak is larger for the thicker film; however, any quantitative assessments are made difficult by the varying sensitivity of Auger peaks

for various elements. Profiling through the thickness of these films shows the phosphorous peak to peak intensity falling to zero within two to four minutes of sputtering time, depending on the density of the oxide layer.

3.   ION SCATTERING, SIMS, CHARACTERISTICS OF ANODIC OXIDE
      FILMS

Ion scattering spectroscopy (Figure 11) shows no specific scattering characteristics other than the expected oxygen and aluminum energy peaks. Phosphorous is a poor scatter in ISS and its energy peak occurs too close to aluminum to be observed.

The SIMS spectrum (Figure 12) shows data from a barrier layer (high refractive index) and a porous layer. With the amplifier sensitivity set at 10^{-7} amperes for both samples it appears the sputtered species from the high refractive index surface are more numerous, with OH^+ and $AlOH^+$ species being present. However, not enough data has been obtained at this time for this to be definitive.

SECTION IV

CONCLUSIONS

The voltage and concentration employed during anodizing aluminum in phosphoric acid has an important influence upon the structure, morphology, and properties of the oxide film. The energetics of the anodizing mechanism are reflected in the data obtained from an ellipsometer. These results establish that a good correlation exists between the refractive index and the nonporous oxide that forms initially at the anode, and the apparent refractive index and the growth of the porous oxide on the nonporous layer. However, due to the affect of the porous structure of the oxide on κ, an element of subjectivity is inherent in these data obtained for thicknesses greater than 1000 Å. This makes it very difficult to determine the type of aluminum oxide compound formed on the anode by ellipsometry. The nonporous, dense, barrier layer should lend itself to the protection of the bulk aluminum from a corrosive environment. The data obtained from this study shows the barrier layer increases in thickness from 330 to 860 Å as concentration and voltage increases. A barrier layer of approximately 150 Å will be generated by the currently used anodizing parameters (10V, 1.0M, 20 minutes).

The AES and positive SIMS techniques appear to have value in these studies. The AES technique has the ability to make a quick estimate of oxide thickness, based on appropriate standards, and the quality of the oxide layer from the elements detected. Using He as the scattering ion, ISS is strictly a first surface layer technique. We were careful to keep our surfaces clean, so for this particular study, ISS was not very informative.

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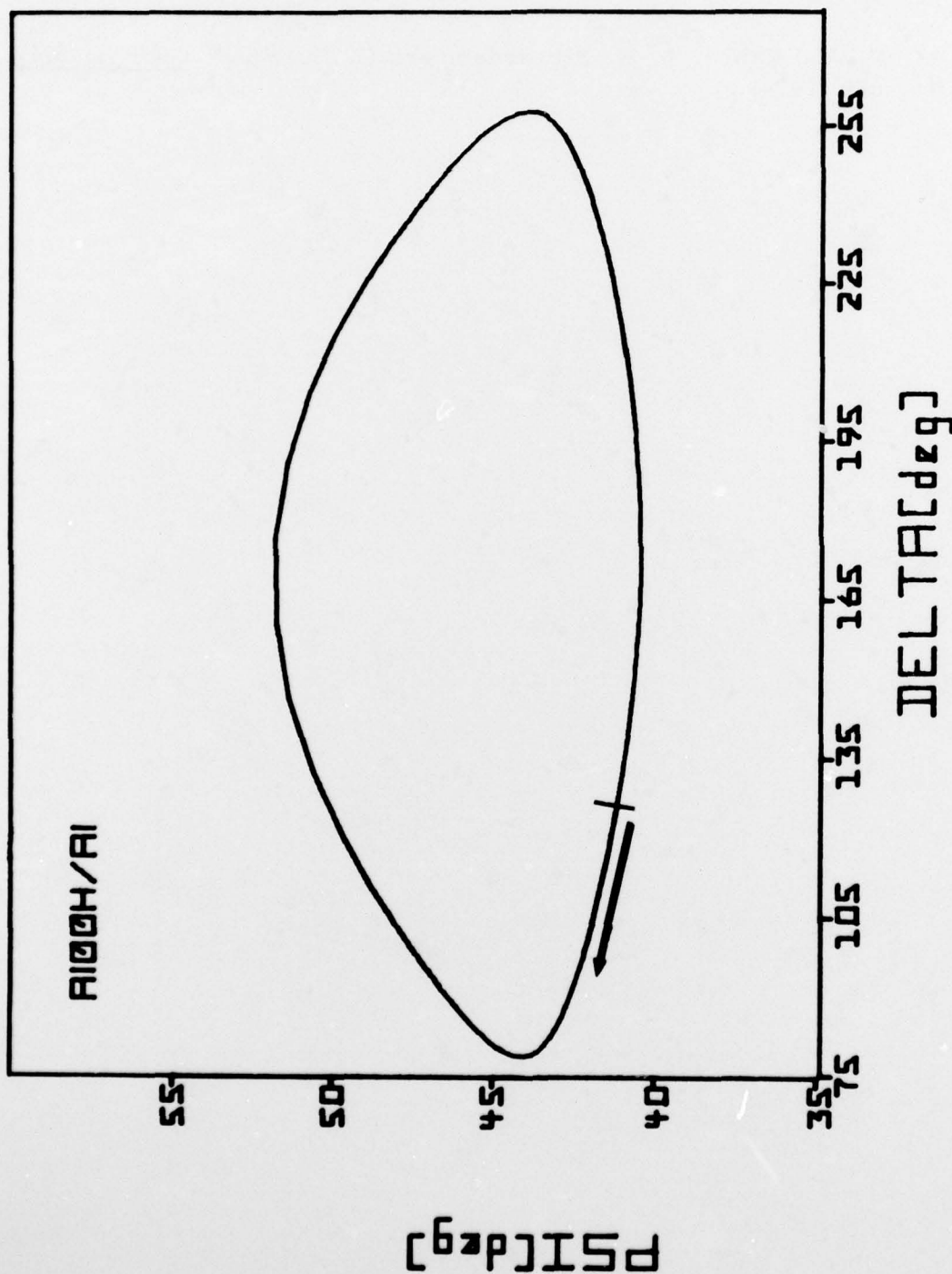   16, 689 (1976).

Figure 1. Ellipsometry Results for Anodization of Aluminum Films in 2% Phthalic Acid: $\eta_f = 1.65$ (boehmite); $\eta_s = 0.8338$, $\kappa = 5.8372$.
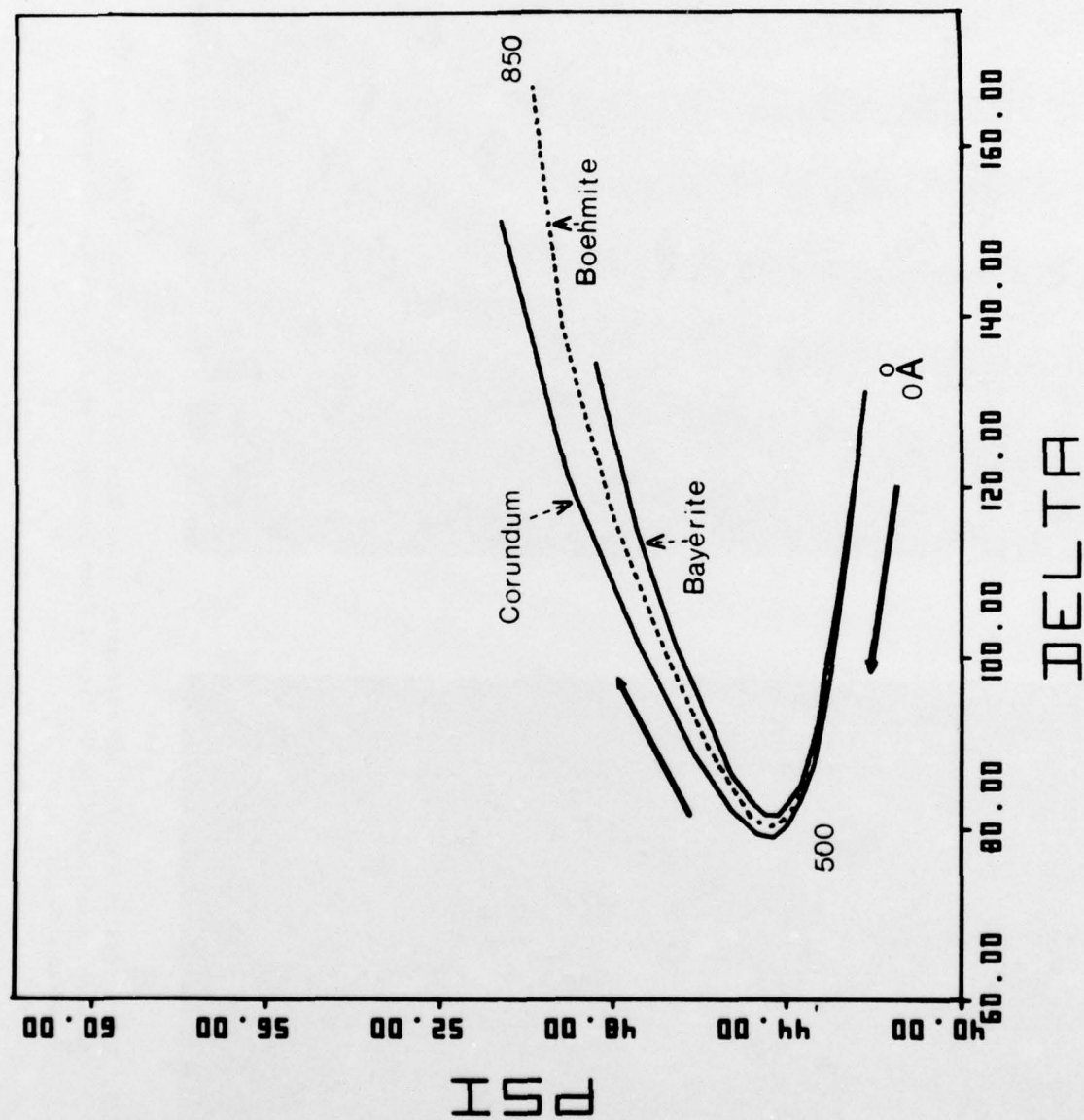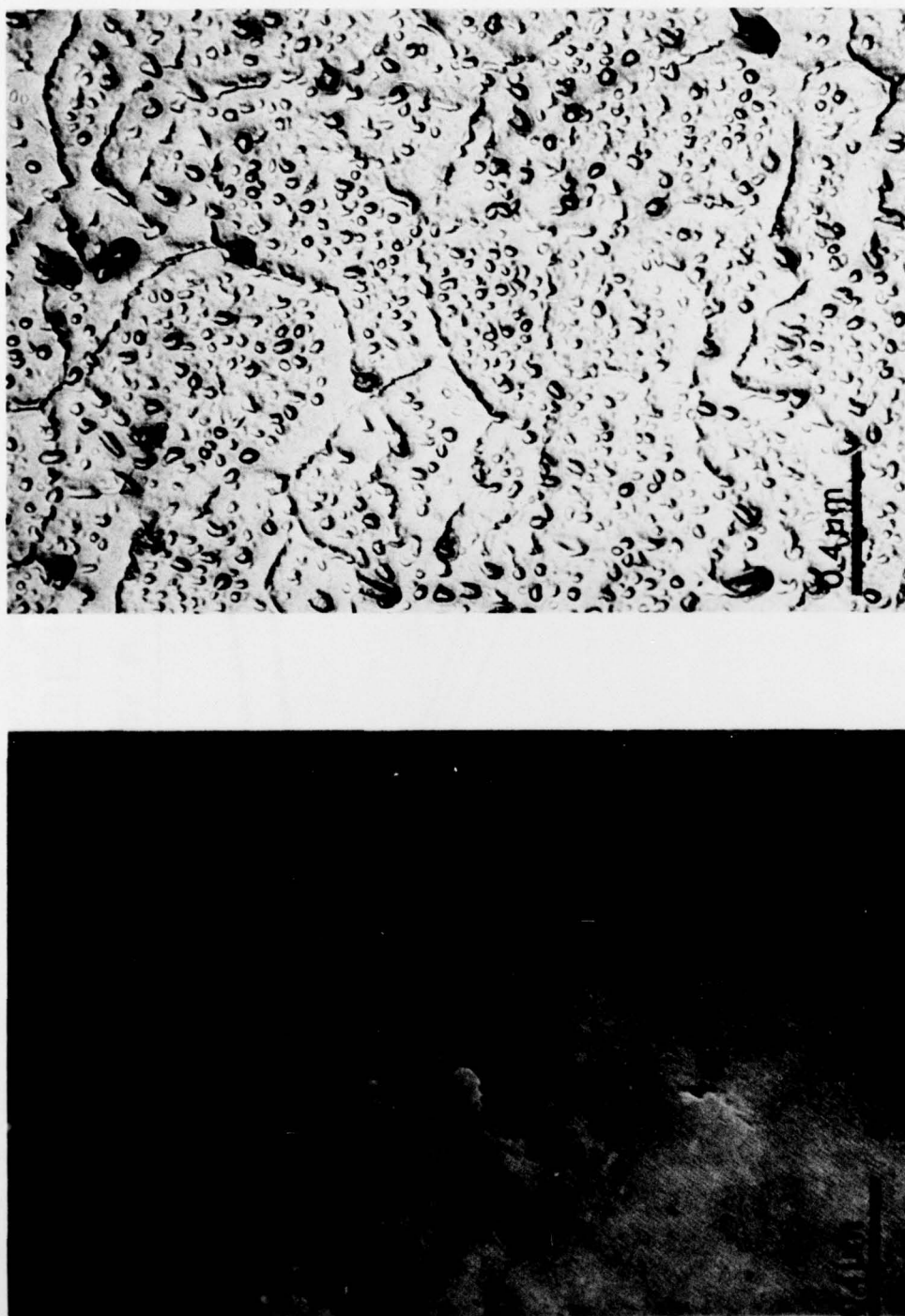
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Figure 2. Δ, ψ Plot for Films of Bayerite, Boehmite, and Corundum on Aluminum Substrate.

a   b

Figure 3. Transmission Electron Micrographs: a) Surface of Film Generated by 30V, 0.1M, 5-Second Anodization; b) Surface of Film Generated by 30V, 0.1M, 300-Second Anodization.

c

d
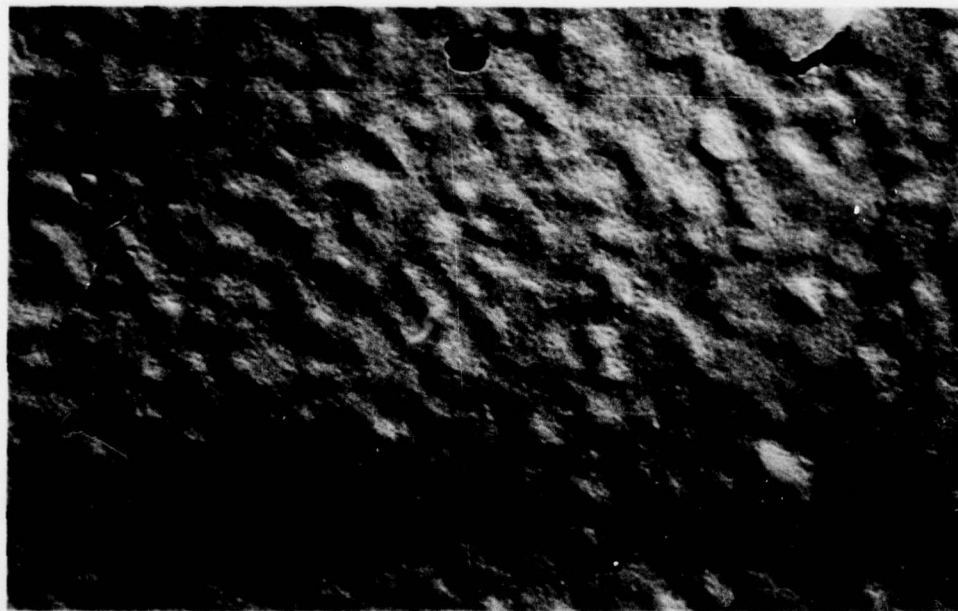
Figure 4. Transmission Electron Micrographs: c) Surface of Film Generated by 60V, 1.0M, 5-Second Anodization; d) Surface of Film Generated by 60V, 1.0M, 300-Second Anodization.
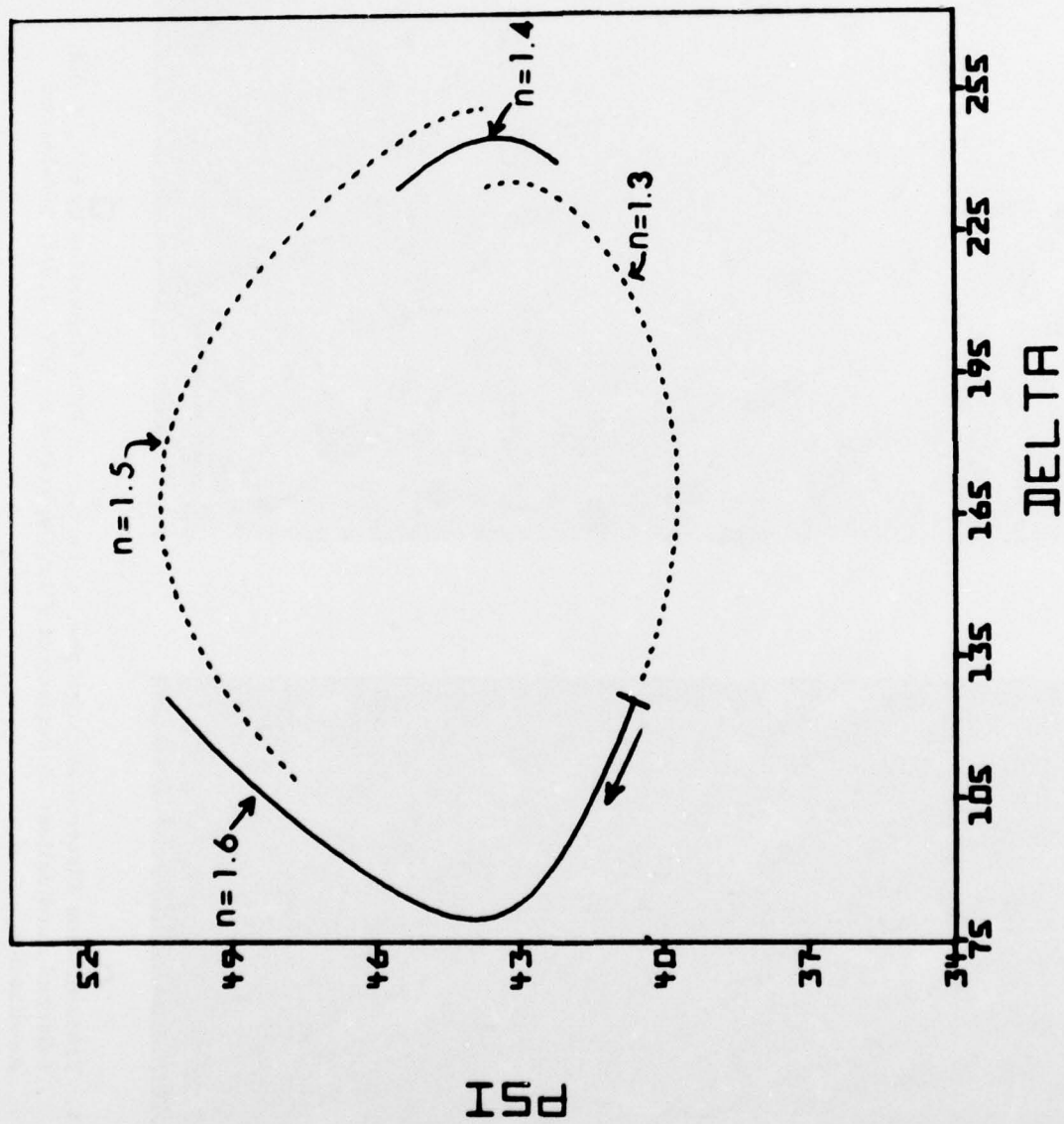
Figure 5. Δ, ψ Plot Showing a Mosaic of Curves with Decreasing Refractive Index.

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U = 1.40(1 - 10.000)
V = 1.40(1 - 10.005)
W = 1.40(1 - 10.010)
X = 1.40(1 - 10.025)

DELTA

PSI
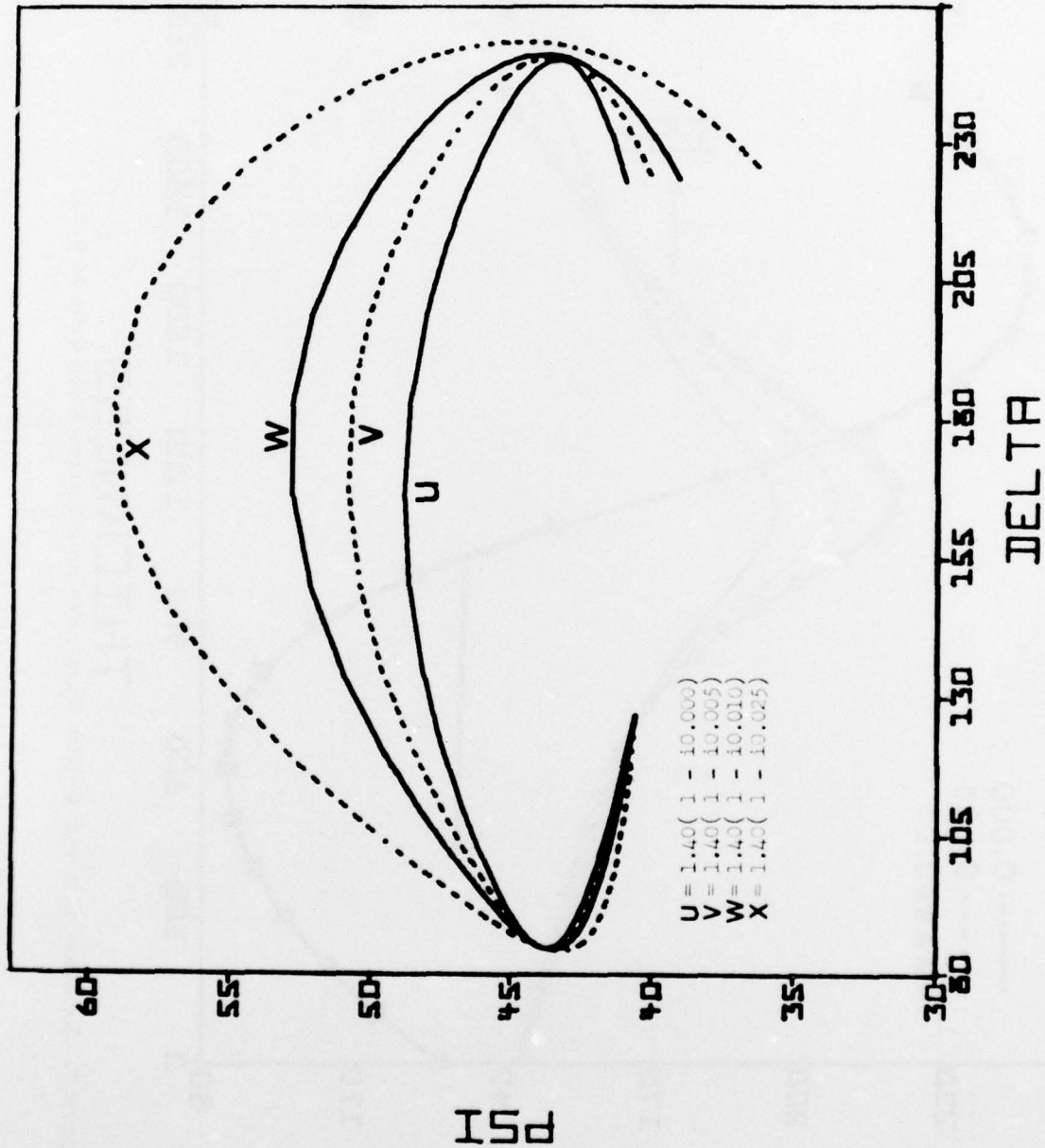
Figure 6. Computed Δ, ψ Curves with η Remaining Constant and κ Varying from 0.00 to 0.025.
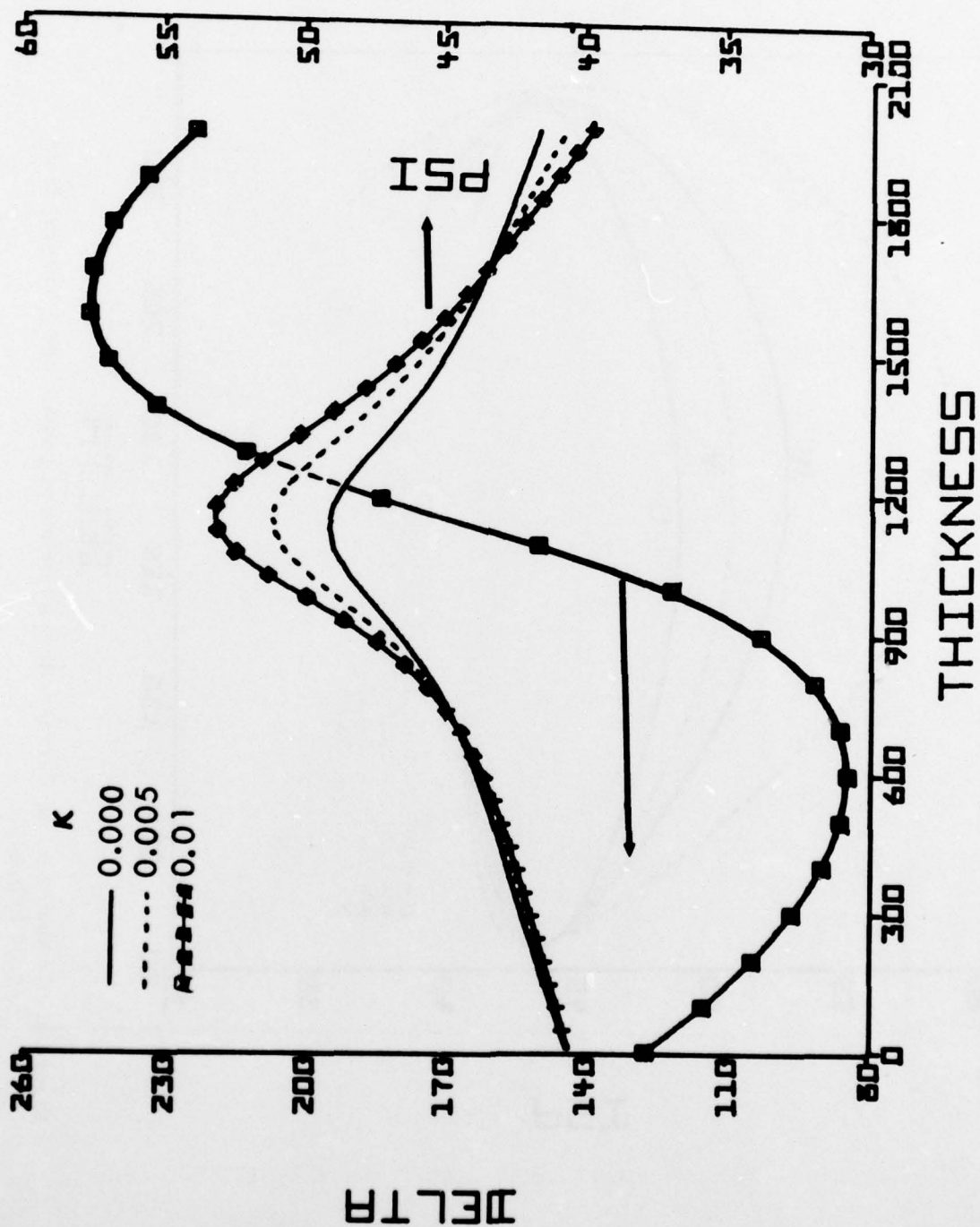
Figure 7. Relation of Δ and ψ with Thickness as κ Varies from 0.00 to 0.01.
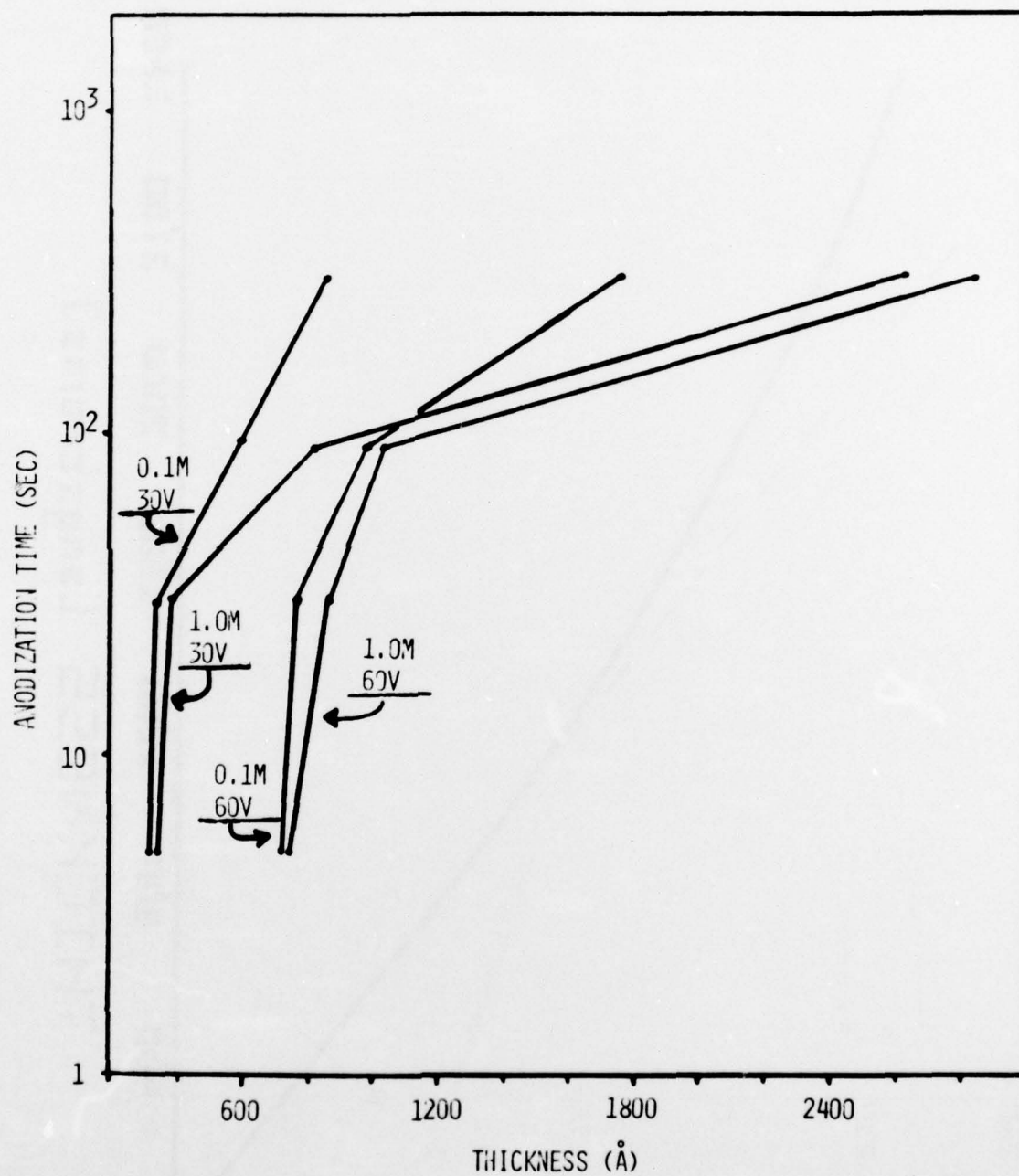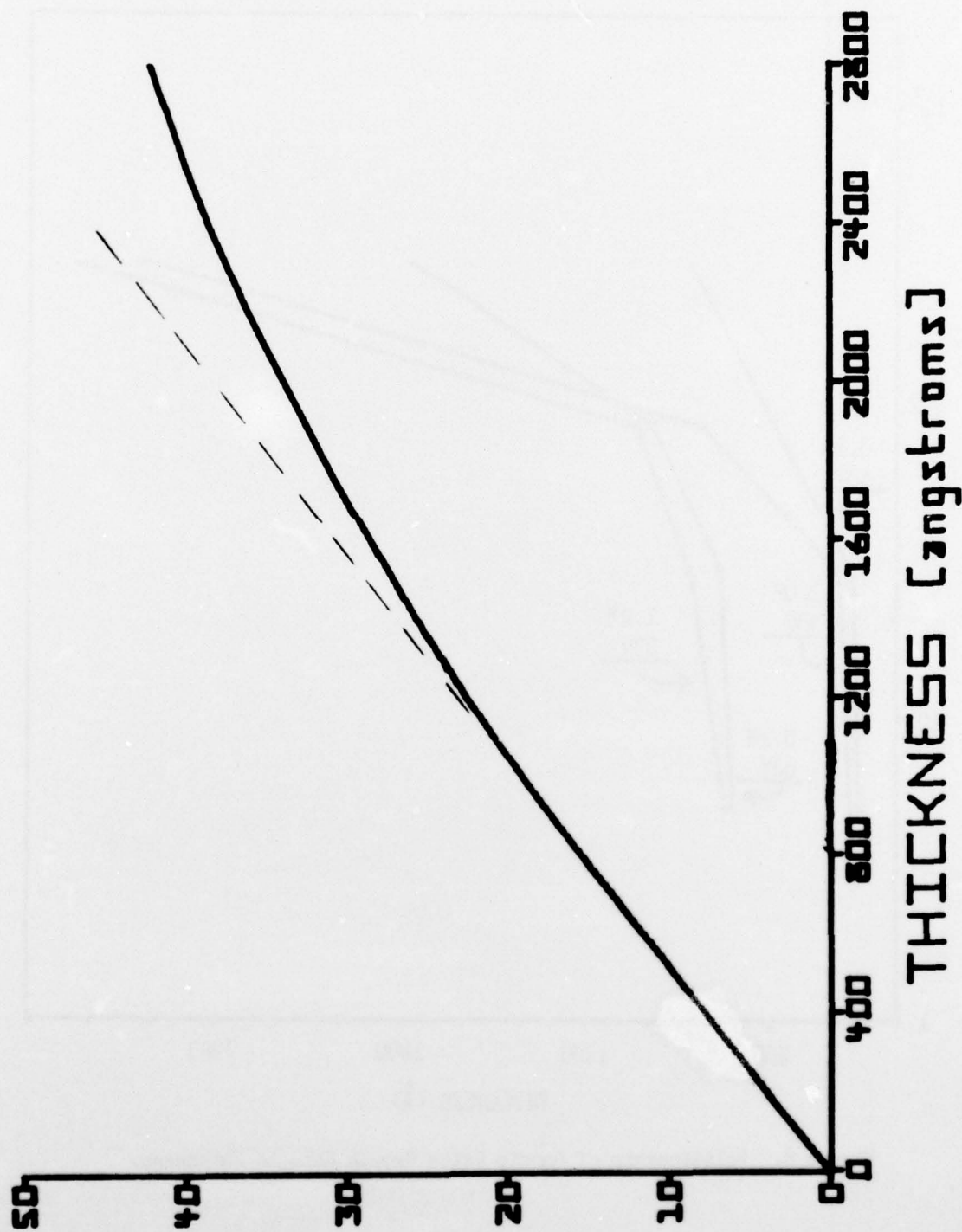
Figure 8. Relationship of Anodic Oxide Growth Rate to Thickness.

THICKNESS [angstroms]

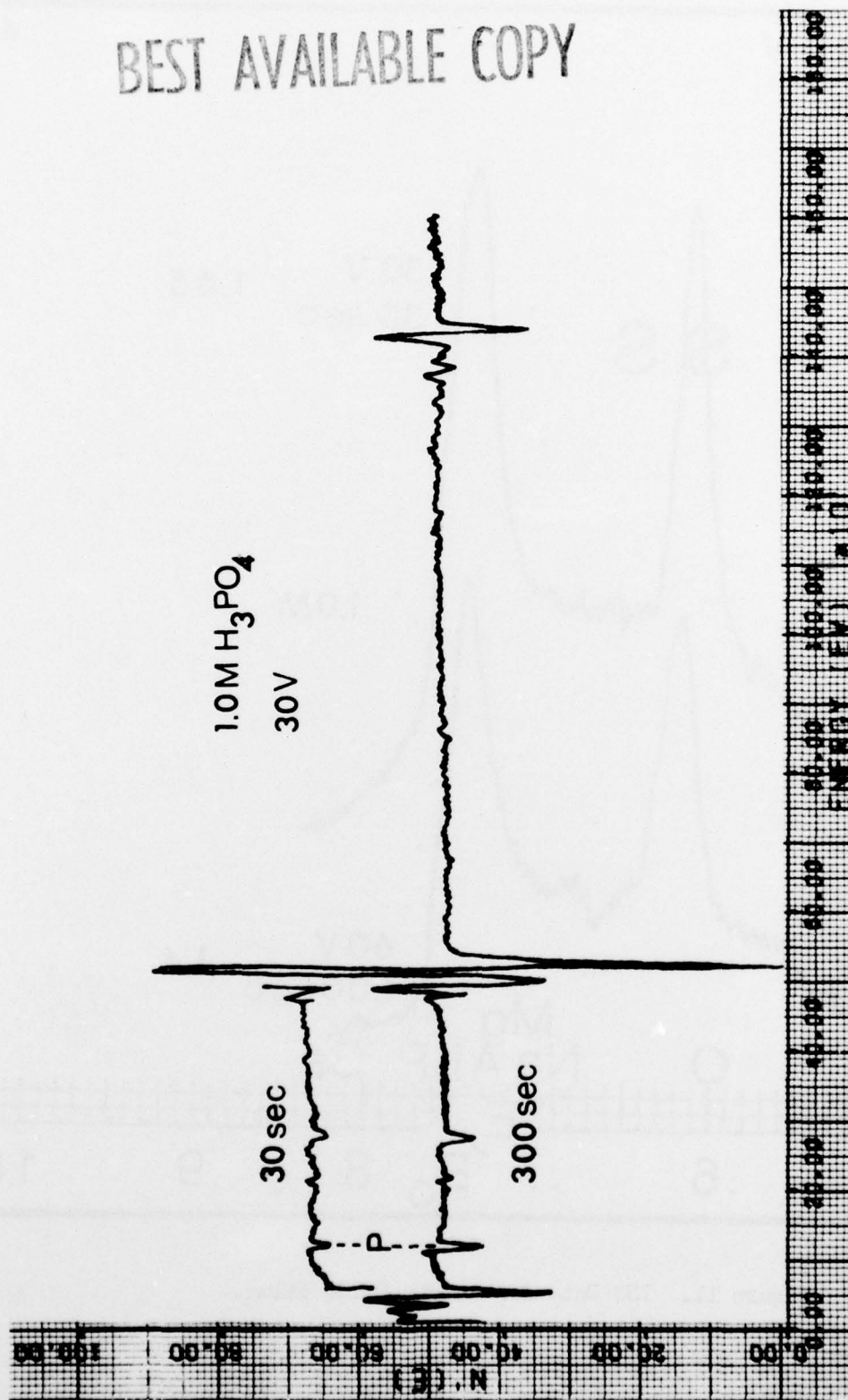Figure 9. Auger Calibration Curve for Phosphoric Acid Anodic Oxides on Aluminum.

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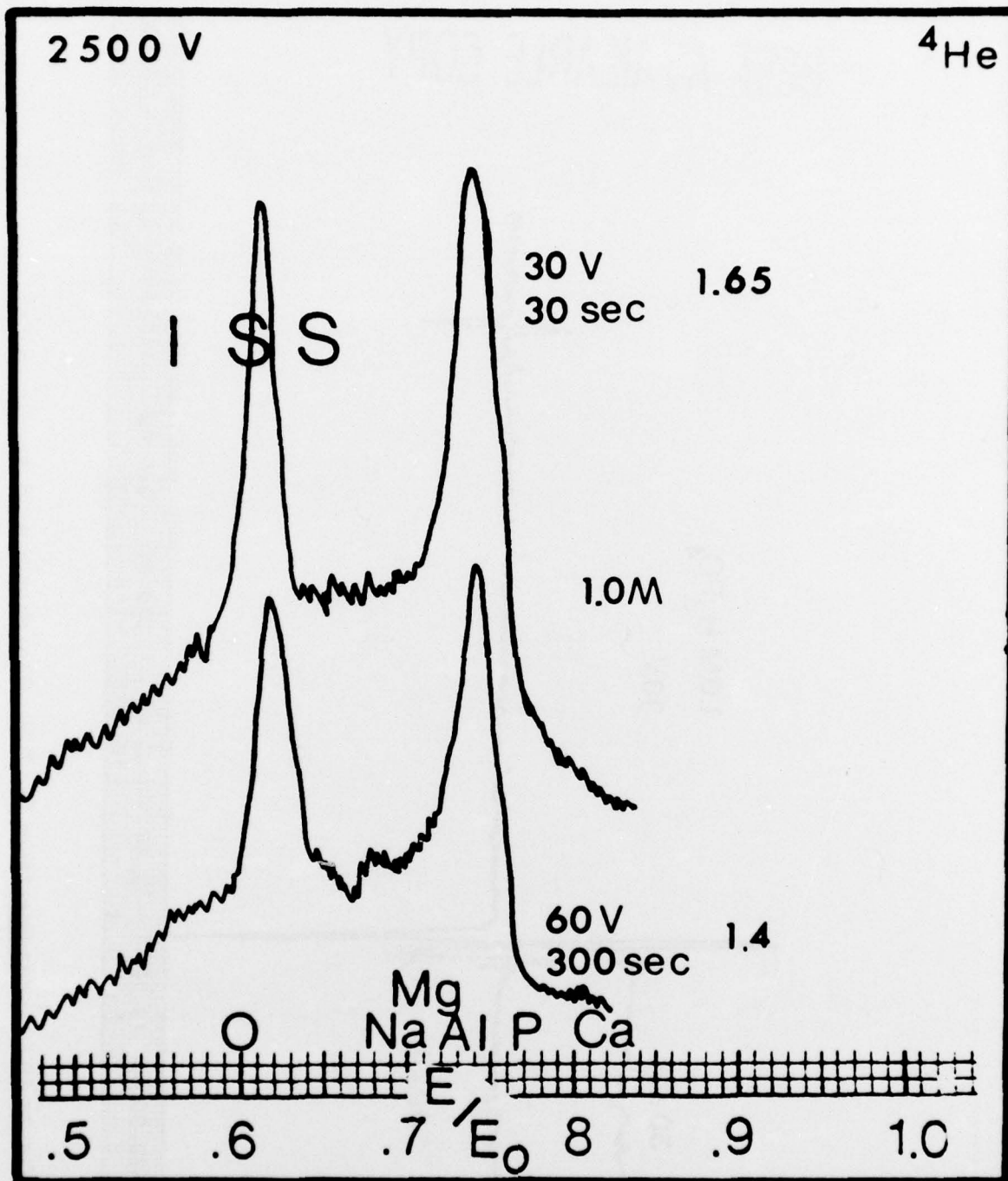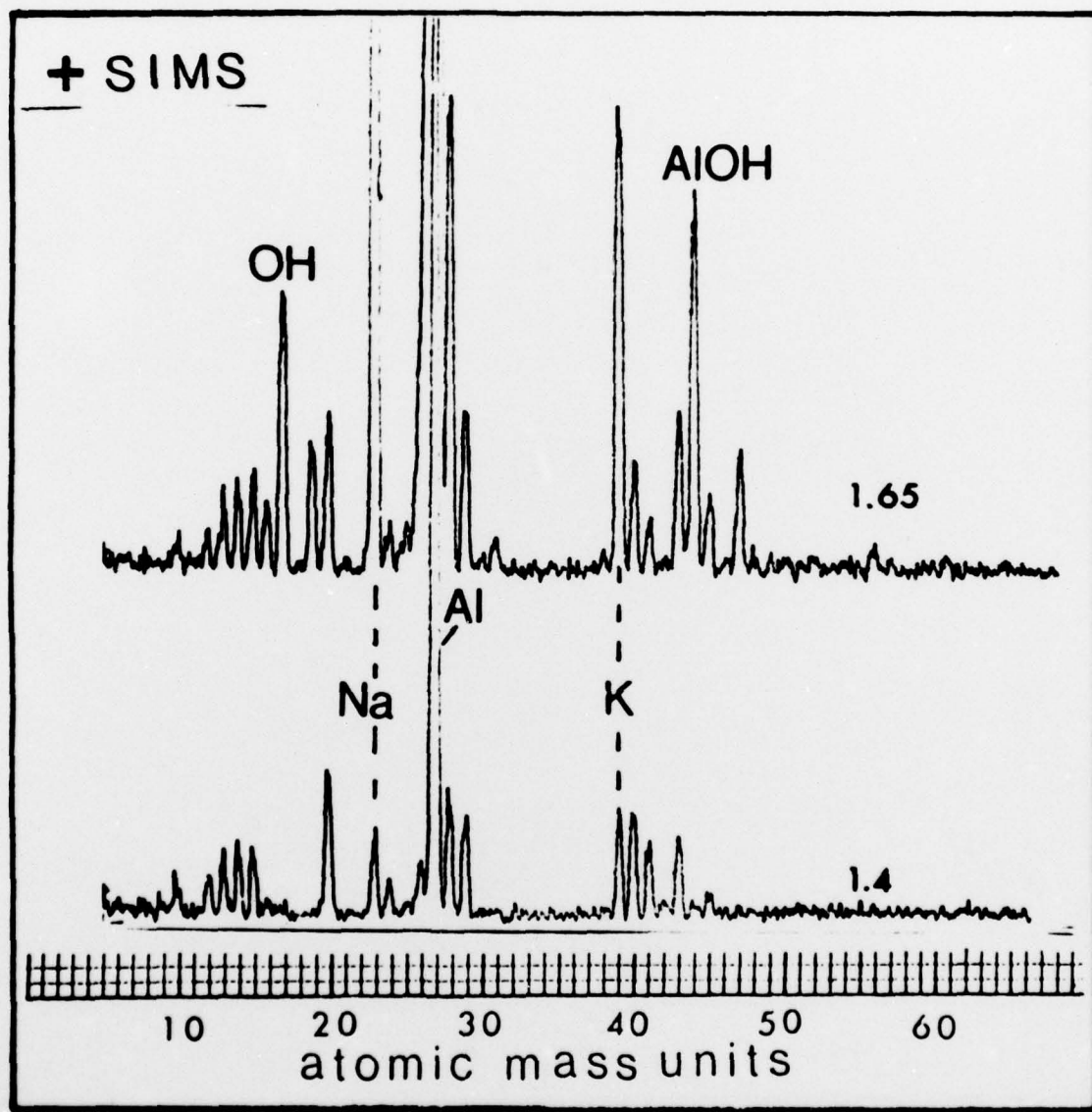Figure 10. Auger Spectrum for 30V, Phosphoric Acid Anodic Oxide.

Figure 11. ISS Data for Anodic Oxide Films.

Figure 12. SIMS Data for Anodic Oxide Films.